

# Space-Time Correlations in the Orientational Order Parameter and the Orientational Entropy of Water

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## ABSTRACT

We introduce the spatial correlation function  $C_Q(r)$  and temporal autocorrelation function  $C_Q(t)$  of the local tetrahedral order parameter  $Q \equiv Q(r, t)$ . Using computer simulations of the TIP5P model of water, we investigate  $C_Q(r)$  in a broad region of the phase diagram. First we show that  $C_Q(r)$  displays anticorrelation at  $r \approx 0.32\text{nm}$  at high temperatures  $T > T_W \approx 250\text{ K}$ , which changes to positive correlation below the Widom line  $T_W$ . Further we find that at low temperatures  $C_Q(t)$  exhibits a two-step temporal decay similar to the self intermediate scattering function, and that the corresponding correlation time  $\tau_Q$  displays a dynamic crossover from non-Arrhenius behavior for  $T > T_W$  to Arrhenius behavior for  $T < T_W$ . Finally, we define an orientational entropy  $S_Q$  associated with the *local* orientational order of water molecules, and show that  $\tau_Q$  can be extracted from  $S_Q$  using an analog of the Adam-Gibbs relation.

The local structure around a water molecule arising from the vertices formed by four nearest neighbors is approximately *tetrahedral*. The degree of tetrahedrality [1, 2, 3] can be quantified by the local tetrahedral order parameter  $Q$  [4, 5, 6, 7, 8]. Spatial fluctuations in  $Q$  suggest a high degree of orientational heterogeneity. The distribution of  $Q$  is bimodal,

centered around less tetrahedral and more tetrahedral values of  $Q$ . Upon decreasing temperature, the high-tetrahedrality peak grows, suggesting that the local structure of water becomes much more tetrahedral at low enough temperatures [9, 10].

Water has been hypothesized to belong to the class of polymorphic liquids, phase separating—at sufficiently low temperatures and high pressures—into two distinct liquid phases: a high density liquid (HDL) with smaller  $Q$  and a low density liquid (LDL) with larger  $Q$  [11]. The co-existence line separating these two phases terminates at a liquid-liquid (LL) critical point. The locus of maximum correlation length in the one-phase region is called the Widom line  $T_W \equiv T_W(P)$ , near which different response functions such as isobaric heat capacity  $C_P$  and isothermal compressibility  $K_T$  display maxima. Recent neutron scattering experiments [12] and computer simulations [13] show that the dynamics of water changes from non-Arrhenius for  $T > T_W$  to Arrhenius for  $T < T_W$ .

In this paper, we ask how the orientational order and its spatio-temporal correlations change upon crossing the Widom line. To this end, we introduce the spatial correlation function  $C_Q(r)$  and the temporal autocorrelation function  $C_Q(t)$  for the local orientational order of water, which can also be applied to study other locally tetrahedral liquids such as silicon [14, 15], silica [16], phosphorus [17]; all of which have also been found to display some of the water-like anomalies. To this end, we perform molecular dynamics (MD) simulations of  $N = 512$  waterlike molecules interacting via the TIP5P potential [18, 19], which exhibits a liquid-liquid (LL) critical point at  $T_C \approx 217$  K and  $P_C \approx 340$  MPa [19, 20]. We carry out simulations in the  $NPT$  ensemble at atmospheric pressure ( $P = 1$  atm) for temperatures  $T$  ranging from 320 K down to 220 K.

To quantify the local degree of orientational order, we calculate the local tetrahedral order parameter [4]

$$Q_k \equiv 1 - \frac{3}{8} \sum_i^3 \sum_{j=i+1}^4 \left[ \cos \psi_{ikj} + \frac{1}{3} \right]^2, \quad (1)$$

where  $\psi_{ikj}$  is the angle formed by the molecule  $k$  and its nearest neighbors  $i$ , and  $j$ . The average value  $\langle Q \rangle \equiv (1/N) \sum_k Q_k$  increases with decreasing  $T$ , and saturates at lower  $T$ , while  $|d\langle Q \rangle/dT|$  has a maximum at the Widom line  $T_W \approx 250$  K [9, 10].

To characterize the spatial correlations of the local order parameter we find all the pairs of molecules  $i$  and  $j$  whose oxygens are separated by distances belonging to the interval

$[r - \Delta r/2, r + \Delta r/2]$ . The number of such pairs is

$$N(r, \Delta r) = \sum_{ij} \delta(r_{ij} - r, \Delta r), \quad (2)$$

where  $r_{ij}$  is the distance between the oxygens of molecules  $i$  and  $j$ . The sum is taken over all molecules in the system and

$$\delta(r_{ij} - r, \Delta r) = \begin{cases} 1 & \text{if } |r - r_{ij}| < \Delta r/2 \\ 0 & \text{otherwise.} \end{cases} \quad (3)$$

For  $\Delta r \rightarrow 0$ ,  $\delta(r_{ij} - r, \Delta r) \rightarrow \delta(r_{ij} - r)\Delta r$  where  $\delta(r_{ij} - r)$  is the Dirac  $\delta$ -function.  $N(r, \Delta r)$  can be approximated as

$$N(r, \Delta r) = 4\pi r^2 N g_{OO}(r) \rho \Delta r. \quad (4)$$

where  $N$  is the total number of molecules in the system,  $g_{OO}(r)$  is the oxygen-oxygen pair correlation function, and  $\rho$  is the number density.

Next we find the local order parameters  $Q_i$  and  $Q_j$  for all such pairs of molecules and compute their mean

$$Q(r) \equiv \langle Q \rangle_r \equiv \frac{\sum_{ij} Q_i \delta(r_{ij} - r, \Delta r)}{N(r_{ij} - r, \Delta r)}, \quad (5)$$

their variance

$$\sigma_Q^2(r) \equiv \langle Q^2 \rangle_r - \langle Q \rangle_r^2 \equiv \sum_{ij} \frac{Q_i^2 \delta(r_{ij} - r, \Delta r)}{N(r_{ij} - r, \Delta r)} - \langle Q \rangle_r^2, \quad (6)$$

and covariance

$$\langle Q_i Q_j \rangle_r \equiv \sum_{ij} \frac{Q_i Q_j \delta(r_{ij} - r, \Delta r)}{N(r_{ij} - r, \Delta r)}. \quad (7)$$

Finally we introduce the spatial correlation function of the local tetrahedrality  $Q$

$$C_Q(r) \equiv \frac{\langle Q_i Q_j \rangle_r - \langle Q \rangle_r \langle Q \rangle_r}{\sigma_Q^2(r)}. \quad (8)$$

In Figs. 1(a) and 1(b), we show  $Q(r)$  and  $\sigma_Q^2(r)$  for different temperatures and atmospheric pressure. The behavior of  $Q(r)$  and its variance  $\sigma_Q^2(r)$  as a function of the distance  $r$  has a clear physical meaning. For the molecules separated by 0.32 nm,  $Q(r)$  has a deep minimum characterizing the distortion of the first tetrahedral coordination shell of the four nearest neighbors by the intrusion of a “fifth neighbor” [21]. Conversely, the quantity  $\sigma_Q^2(r = 0.32\text{nm}) - \sigma_Q^2(\infty)$  for such molecules dramatically increases upon decreasing temperature [see Fig. 1(c)], and has a maximum at  $T \approx 246$  K which is approximately equal to the ambient pressure value of  $T_W$  ( $\approx 250$  K for the TIP5P model) reported in Refs. [10, 13]. In Fig. 1(d),

we show  $C_Q(r)$  for different temperatures for  $P = 1$  atm.  $C_Q(r)$  has positive maxima at positions of the first and second peaks in the oxygen-oxygen pair correlation function, suggesting that the molecules located at the tetrahedral positions are strongly correlated in their  $Q$  values. Water molecules separated by  $r \approx 0.32\text{nm}$  exhibit weak anticorrelation in local tetrahedral order at high temperatures, which changes to positive correlations upon decreasing temperature below  $T_W$ .

To study the time development of local tetrahedral orientational order parameter, we introduce the time autocorrelation function

$$C_Q(t) \equiv \frac{\langle Q(t)Q(0) \rangle - \langle Q \rangle^2}{\langle Q^2 \rangle - \langle Q \rangle^2}. \quad (9)$$

In Fig. 2(a) we show  $C_Q(t)$  for different temperatures. The decay of  $C_Q(t)$  is reminiscent of the decay of the self intermediate scattering function. The long time behavior of  $C_Q(t)$  is exponential at high  $T$ , but at low  $T$  can be fit with a stretched exponential  $\exp[-(t/\tau)^\beta]$ , where  $0 < \beta < 1$ . We define the correlation time  $\tau_Q$  as the time required for  $C_Q(t)$  to decay by a factor  $e$ . Figure 2(b) shows the values of  $\tau_Q$  as function of  $1/T$  on an Arrhenius plot. The behavior of  $\tau_Q$  is non-Arrhenius at high temperatures and can be fit by a power law  $(T - T_{\text{MCT}})^{-\gamma}$  where  $T_{\text{MCT}} \approx 235$  is the mode coupling temperature [13, 22]. At low  $T$ ,  $\tau_Q$  deviates from the power-law fit and becomes Arrhenius. This crossover in relaxation of local orientational order occurs near  $T_W$ .

Since  $Q$  measures the local orientational order, it must contribute to the entropy of the system. We next derive an expression for this “orientational entropy”  $S(Q_1, Q_2, \dots, Q_N)$ , which we define to be the logarithm of the number of states corresponding to the interval between  $(Q_1, Q_2, \dots, Q_N)$  and  $(Q_1 + \Delta Q_1, Q_2 + \Delta Q_2, \dots, Q_N + \Delta Q_N)$ . According to Eq. (1),  $8(1 - Q_k)/3 = \text{const}$  defines a surface of a six-dimensional hypersphere of radius  $\sqrt{8(1 - Q_k)/3}$  in the space defined by the six tetrahedral angles  $\psi_{ikj}$  of Eq. (1). Hence we assume that the number of states between  $Q_k$  and  $Q_k + \Delta Q_k$  of molecule  $k$  scales as  $(1 - Q_k)^{5/2} \Delta Q_k$ . We assume that the order parameters of each molecule is independent, an assumption justified by the small value of  $C_Q(r)$  studied. Thus we can define the number of states  $\Omega(Q_1, Q_2, \dots, Q_N)$  in the interval between  $(Q_1, Q_2, \dots, Q_N)$  and  $(Q_1 + \Delta Q_1, Q_2 + \Delta Q_2, \dots, Q_N + \Delta Q_N)$  as the product

$$\Omega(Q_1, Q_2, Q_3, \dots, Q_N) \equiv N \Omega_0 \prod_{k=1}^N (1 - Q_k)^{5/2}, \quad (10)$$

where  $\Omega_0 = \text{const.}$  Hence the orientational entropy of the entire system is given by

$$S(Q_1, Q_2, Q_3, \dots, Q_N) \equiv NS_0 + \ln \prod_{k=1}^N (1 - Q_k)^{\frac{5}{2}} \equiv NS_0 + \frac{5}{2} \sum_{k=1}^N \ln(1 - Q_k). \quad (11)$$

where  $S_0 = \ln \Omega_0$ . If  $P(Q, T)$  is the distribution of  $Q$  at a given temperature  $T$ , then the orientational entropy  $S_Q(T)$  per particle at temperature  $T$  can be written as

$$S_Q(T) \equiv S_0 + \frac{5}{2} \int_{Q_{\min}}^{Q_{\max}} \ln(1 - Q) P(Q, T) dQ. \quad (12)$$

In Fig. 3 (a), we show that  $S_Q(T) - S_0$  decreases with decreasing temperature as expected.

We further define a measure of “orientational specific heat” as  $C_P^Q(T) \equiv T(\partial S_Q(T)/\partial T)_P$ . Figure 3(b) shows the temperature dependence of  $C_P^Q(T)$  for  $P = 1$  atm.  $C_P^Q(T)$  shows a maximum at  $T \approx 245\text{K} \approx T_W$ , where the total specific heat  $C_P$  has a maximum [10, 13], suggesting that the fluctuations in orientational order reach a maximum at  $T_W(P)$ .

To relate the orientational entropy  $S_Q(T)$  to the orientational relaxation time  $\tau_Q(T)$  associated with the local tetrahedral ordering, we propose the following generalization of the Adam-Gibbs relation between the translational relaxation time and configurational entropy [23, 24],

$$\tau_Q(T) = \tau_Q(0) \exp[A/TS_Q(T)], \quad (13)$$

where  $\tau_Q(0)$  is the orientational relaxation time at very large  $T$ , and  $A$  is a parameter playing the role of activation energy. Accordingly we calculate [Fig. 2(b)]  $\tau_Q(T)$  from  $S_Q(T)$  using Eq. (13) with three free parameters:  $A$ ,  $\tau(0)$ , and  $S_0$ . We find that  $S_0 \approx 4.33$ .

Figure 2(b) is an Arrhenius plot of  $\tau_Q$ , calculated from Eq. (13). The temperature dependence of  $\tau_Q$  is different at low and high temperatures, changing from non-Arrhenius (a  $T$ -dependent slope on the Arrhenius plot) which can be fit by a power law at high temperatures to Arrhenius (a constant slope) at low temperatures [10, 12, 13].

In summary, we have studied the space and time correlations of local tetrahedral order, presumably related to local orientational heterogeneities. We find that the spatial correlation of the the local tetrahedral order is anticorrelated for the molecules separated by  $3.2\text{\AA}$  at high temperatures. This negative correlation changes to positive correlation upon decreasing  $T$  below the Widom temperature  $T_W(P)$ . Further, we define a measure of the orientational entropy  $S_Q$  and find that it well describes orientational relaxation using the Adam-Gibbs relation.

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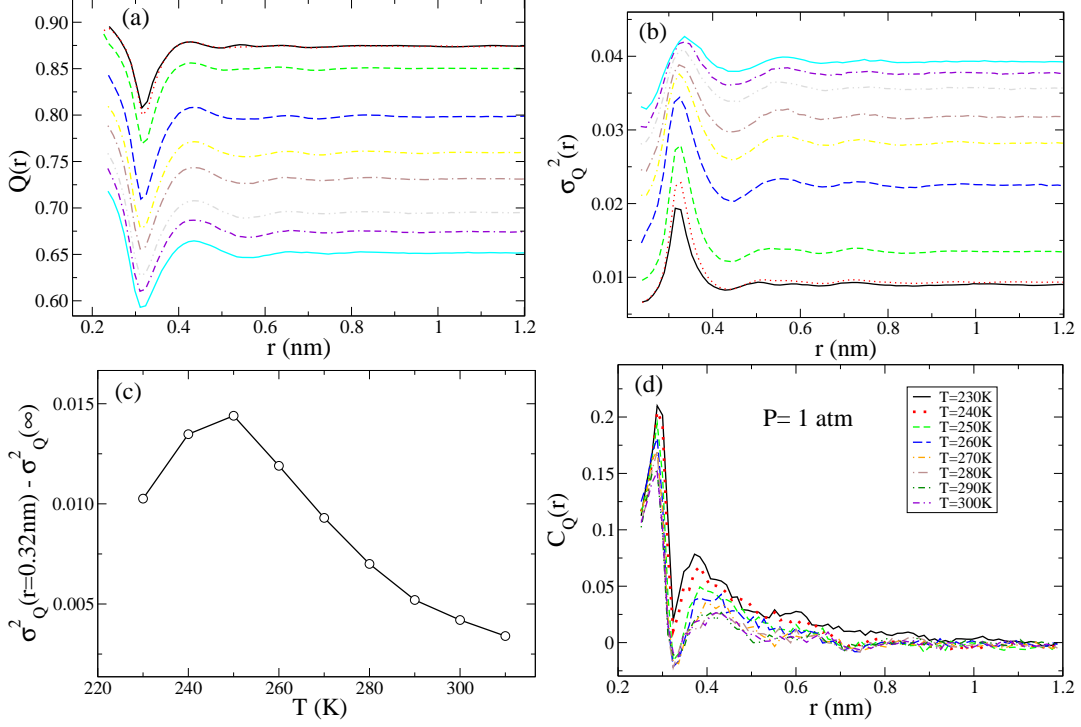


FIG. 1: (color online) (a) The average order parameter  $Q(r)$  and (b) its variance,  $\sigma_Q^2(r)$ , as a function of the distance  $r$ . (c) Temperature dependence of  $\sigma_Q^2(r = 0.32\text{nm}) - \sigma_Q^2(\infty)$  shows a maximum at the Widom temperature, suggesting the local fluctuations in  $Q$  at the fifth-neighbor distance increases upon decreasing temperature and has a maximum at the Widom line. (c) Spatial correlation function  $C_Q(r)$  of orientational order parameter  $Q$  [Eq. (1)], at various temperatures for pressures  $P = 1$  atm.  $C_Q(r)$  has positive peaks at the positions of the nearest neighbor peaks in oxygen-oxygen pair correlation function  $g_{\text{OO}}(r)$ . A negative minimum at the fifth neighbor distance  $r \approx 0.32$  nm for high  $T$  implies that the local tetrahedral order of a central molecule and its fifth neighbor are anticorrelated at  $T > 250\text{K}$ . Interestingly the anticorrelation at  $r = 0.32$  nm changes to positive correlations upon crossing below the Widom line around  $T_W \approx 250$  K.



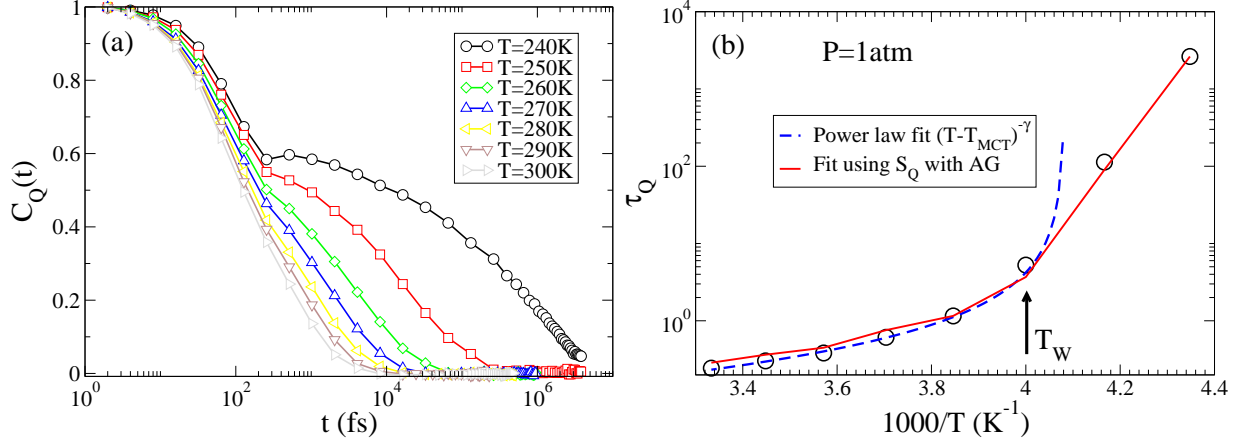


FIG. 2: (color online) (a) Autocorrelation function  $C_Q(t)$  of orientational order parameter  $Q$  at various temperatures.  $C_Q(t)$  is exponential at high temperatures but displays a visible two step decay at low temperatures. (b) Correlation time  $\tau_Q$  extracted from  $C_Q(t)$ . Solid line is the fit using the Adam-Gibbs relation [Eq. (13)] between the orientational entropy  $S_Q(T)$ , and the orientational relaxation time  $\tau_Q$ . The dotted lines in (b) is the power law fit  $(T - T_{\text{MCT}})^{-\gamma}$ . Behavior of  $\tau_Q$  deviates from the power law fit and has a crossover to Arrhenius behavior at low temperature near the same temperature  $T_W$  where the response functions have maxima, which we identify with crossing the Widom line  $T_W$ .

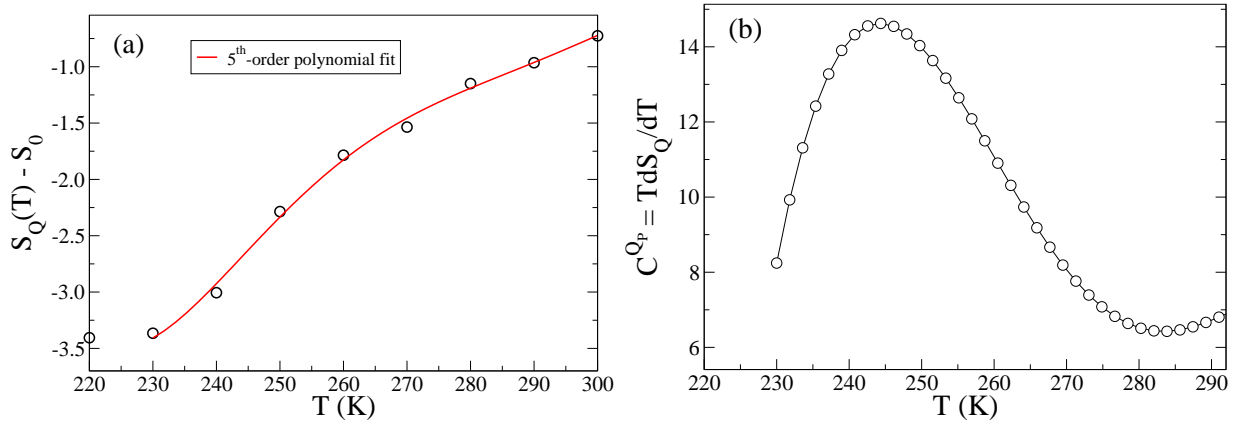


FIG. 3: (color online) Temperature dependence of (a) orientational entropy  $S_Q(T)$ , defined in Eq. (11), and (b) orientational specific heat  $C_P^Q = T (\partial S_Q / \partial T)_P$ , which has a maximum around the same temperature,  $T \approx 246$  K  $\approx T_W$ , where the total specific heat  $C_P$  has a maximum. Solid line in (a) is a 5<sup>th</sup>-order polynomial fit through the data which is used to generate (b)